(12) **EUROPEAN PATENT APPLICATION**

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(54) Process for increasing the cetane number of diesel fuels.

(57) The cetane number of a middle distillate fuel fraction is increased by contacting said fraction with oxygen or oxidant, in the presence of a catalyst, for a time sufficient to increase the cetane number. The catalyst selectively oxidizes benzylic carbon atoms present in the fuel to ketones. The fuel is preferably hydrorefined before being selectively oxidized.

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PROCESS FOR INCREASING THE CETANE NUMBER OF DIESEL FUELS.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a process for improving the cetane number of middle distillate fuels. More particularly, this invention relates to a catalytic process for improving the cetane number of a hydrotreated diesel fuel containing aromatic and hydroaromatic compounds by selectively oxidizing, in the presence of a suitable catalyst, at least a portion of the benzylic carbon atoms present in said compounds.

BACKGROUND OF THE DISCLOSURE

The cetane number of a middle distillate diesel fuel is a measure of the ignition quality of the fuel. Fuels having a low cetane number frequently may be characterized by poor cold weather starting, long ignition delays, increased combustion noise and even misfiring.

Methods of improving the cetane number of fuels have taken on increasing importance as the refinery product slate has changed and as the quality of the crude feedstocks has declined. The heavier crudes currently being processed normally produce less virgin middle distillate, and the distillate which is produced tends to be of a lower cetane quality. Moreover, the decline in residual fuel oil consumption often requires that at least a portion of the bottoms produced be upgraded by cracking. This upgraded middle distillate frequently is high in aromatic content, resulting in a low cetane rating. In addition, the rate of consumption of gasoline in many industrial countries has been relatively flat in recent years, while the consumption of diesel fuel and jet fuel has been increasing. To increase jet fuel production, frequently kerosene rich cuts are blended with the jet fuel. Addition of kerosene rich cuts, which have high cetane blending numbers, to the jet fuel necessarily decreases the quantity of kerosene available for use in diesel fuels. These factors have combined to make it increasingly important to maximize the quantity of middle distillate produced and to improve the cetane rating of the middle distillate fuels.

A number of different approaches have been taken in order to improve the cetane rating of middle distillate fuels. One method has been to blend middle distillates having low cetane numbers with other feedstocks having higher cetane numbers. Another method has involved the addition of cetane improvers, such as alkyl nitrates, in order to raise the cetane number of the distillate. However, one does not always have readily available feedstocks of high cetane rating to blend with middle distillate fuels. In general, high cetane rating distillates are used as fuels in more demanding applications, such as jet fuels. Addition of cetane improvers, such as alkyl nitrates is not always desirable, since one may incur the possible loss of desirable fuel stability properties.

A number of different oxygenation processes have been suggested in the past. Thus, U. S. patent 2,521,698 discloses a partial oxidation of hydrocarbon fuels to improve their cetane ratings. This patent discloses that the fuel should have a relatively low aromatic ring content and a high paraffinic content. U. S. patent 2,912,313 discloses an increase in cetane number obtained by adding both a peroxide and a dihalo compound to middle distillate fuels. U. S. 2,472,152 discloses a process for improving the cetane number of diesel fractions via oxidation of saturated cyclic hydrocarbon or naphthenic hydrocarbons in said fractions to form naphthenic peroxides. The disclosure suggests that the process may be accelerated in the presence of an oil-soluble metal salt as an initiator, but is preferably accomplished in the presence of an inorganic base. The so-formed naphthenic peroxides are disclosed as being gum initiators. Consequently, gum inhibitors such as phenols, cresols and cresylic acids must be added to the oxidized material to reduce or prevent gum formation. These latter compounds are toxic and carcinogenic.

Finally, U.S. 4,494,961 relates to improving the cetane number of raw, untreated diesel fuel fraction by contacting said fraction at a temperature of from 50 to 350°C and under mild oxidizing conditions with a catalyst which is either i) an alkaline earth metal permanganate, ii) an oxide of a metal of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB or VIII of the periodic table or iii) a mixture of i and ii.

SUMMARY OF THE INVENTION

Those skilled in the art know that middle distillate fuel fractions obtained from various refinery streams contain various aromatic and hydroaromatic hydrocarbon compounds which have benzylic carbon atoms.
5 The present invention relates to a process for increasing the cetane number of middle distillate fuels by selectively oxidizing, in the presence of a catalyst, at least a portion of the benzylic carbon atoms present in said aromatic and hydroaromatic hydrocarbon compounds present in said fuels to ketones. Thus, according to the process of this invention the cetane number of a middle distillate fuel containing benzylic carbon atoms may be increased by contacting said distillate, with oxygen or a suitable oxidant in the presence of a
10 suitable catalyst, for a time sufficient to oxidize at least a portion of the benzylic carbon atoms present therein to form alcohols or ketones. By selective oxidation is meant that of that portion of the benzylic carbon atoms present that are oxidized employing the process of this invention, at least about 85% thereof are oxidized to ketones.

In one embodiment, the raw or untreated distillate fuel fraction will be catalytically hydrotreated or
15 hydrorefined in order to increase the number of benzylic carbon atoms present therein to be selectively oxidized according to the process of this invention. Such hydrorefining also reduces the amount of sulfur and nitrogen present in the fuel.

The temperature employed in the process of this invention must be kept low enough (i.e., no greater than about 200°C) to avoid attack on the much stronger bonds of the primary, secondary and tertiary alkyl
20 carbon-hydrogen bonds of the paraffins and cycloparaffins and the much stronger carbon-hydrogen bonds of the aromatic ring which would reduce the cetane number of the fuel.

The process of this invention may be employed with all or a portion of the middle distillate or desired fuel fraction thereof. In one embodiment, at least a portion of the aromatic and hydroaromatic compounds will be separated from the distillate. Such separation may be accomplished by various means such as
25 extraction, distillation, selective absorption, etc. The separated portion, rich in aromatic and hydroaromatic compounds containing benzylic carbon atoms will then be selectively oxidized according to the process of this invention. All or a portion of the oxidized material may, if desired, be blended with a fraction having a poor cetane rating. This is illustrated, as follows, for the case where the separation is accomplished by extraction.

30 Thus, in one embodiment, at least a portion of the aromatic and hydroaromatic compounds which contain benzylic carbon atoms will be extracted from the distillate. The so-formed extract will then be oxidized by contacting same with oxygen or a suitable oxidant in the presence of a suitable catalyst for a time sufficient to selectively oxidize at least a portion of said aromatic and hydroaromatic compounds at the benzylic carbon atom position to form ketones. At least a portion of the oxidized extract will then be
35 blended back into the extracted distillate to form a middle distillate fuel of improved cetane number.

In another embodiment, at least a portion of an unextracted fuel fraction will be oxidized according to the process of this invention and utilized as a fuel of improved cetane number or blended with an unoxidized fuel fraction to improve its cetane number.

By benzylic carbon atom is meant a carbon atom directly bond to an aromatic ring, but which itself is
40 not a part of an aromatic ring. Illustrative, but non-limiting examples include tetralin which has two benzylic carbon atoms, alkylbenzenes which have at least one benzylic carbon atom and indanes.

DETAILED DESCRIPTION OF THE INVENTION
45

As set forth above, the present invention relates to increasing the cetane number of a middle distillate fuel fraction by contacting said fraction, or at least a portion of said fraction which contains aromatic and hydroaromatic hydrocarbon compounds having benzylic carbon atoms, with oxygen or a suitable oxidizing agent, in the presence of a catalyst, for a time sufficient to oxidize at least a portion of the benzylic carbon
50 atoms present in said fraction to alcohols or ketones.

Those skilled in the art know that middle distillate fuels comprise petroleum refinery hydrocarbon fractions boiling within the general range of about 300-850°F and possess aromatic and hydroaromatic hydrocarbon compounds which contain benzylic carbon atoms. Within this broad fraction are included kerosine and jet fuel fractions and truck, train and marine diesel fuel fractions. The raw, untreated fraction is
55 obtained as a petroleum refinery distillate and comprises various paraffinics, cycloparaffins, hydroaromatic and aromatic compounds, as well as various sulphur and nitrogen containing compounds. At least a portion of the hydroaromatic and other aromatic compounds present in these fractions, particularly the diesel fuel fractions, contain benzylic carbon atoms. The selective oxidation of the benzylic carbon atoms present in

3

these compounds to alcohols and ketones, particularly ketones, has been found to substantially increase their cetane rating. At the same time, it has been found that oxidation of the paraffins and cycloparaffins present in the fuel or oxidation of aromatic or hydroaromatic compounds at non-benzylic carbon positions, such as in the ring to form a phenol, adversely affects the cetane rating of the fuel.

5   Mass spectral and gas-liquid chromatographic analysis have shown that the relatively low temperature oxidation process of this invention selectively oxidizes the benzylic carbon atoms of the aromatic and hydroaromatic components present in the fuel fraction to the corresponding ketone or alcohol. By selective oxidation is meant that of that portion of the benzylic carbon atoms present that are oxidized employing the process of this invention, at least about 85%, and more generally at least about 90% thereof are oxidized to
10   ketones.

The process of this invention can be illustrated by the oxidation of tetralin to tetralone, according to the reaction sequence set forth below. Tetralin has two benzylic carbon atoms on the saturated ring at the 1 and 4 position. However, only the reaction with the carbon atom in the 1 position is illustrated here.

15

Tetralin   Tetralin   Tetralone
                    Hydroperoxide

20
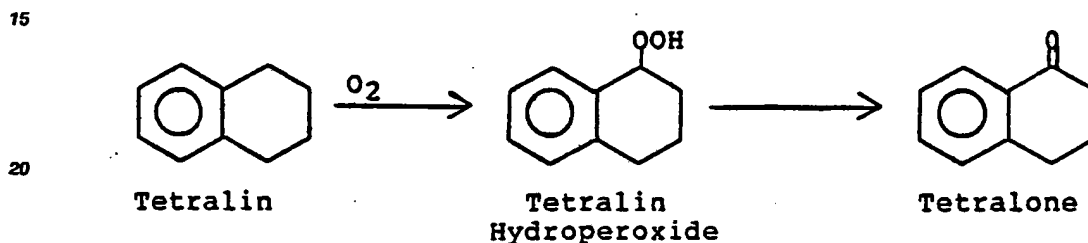
The tetralin is initially oxidized to the hydroperoxide at one of the benzylic carbon atoms. However, it
25   has been found that in the absence of a catalyst very little (i.e., about 5%) of the hydro peroxide will convert to the ketone. Instead, a relatively large number of other oxygenated products will be formed which do not improve cetane number. Ketones are preferred over alcohols as the oxygenated products of the benzylic carbon atoms, because the alcohols are more susceptible to separation, water retention, etc.

It will be shown below that such ketones and alcohols, particularly ketones, have a much greater cetane
30   number than the same compounds wherein the benzylic carbon atoms have not been so oxidized.

Illustrative, but non-limiting examples of benzylic carbon containing aromatic and hydroaromatic hydrocarbon compounds present in middle distillate fuel fractions include alkylbenzenes, alkylnaphthalenes, indanes, indenes, acenaphthenes, 1,2,3,4 tetrahydronaphthalenes, hydrophenanthrenes, and the like. Tables 1, 3, 4 and 5 below set forth the change in cetane number achieved by oxidizing a benzylic carbon present
35   in various aromatic and hydroaromatic hydrocarbon compounds to alcohols and ketones. Thus, the specific benzylic carbon atom containing compounds set forth in these tables further illustrate such compounds suitable for use in the process of this invention. In Table 1, all of the compounds except the biphenyls contain at least one benzylic carbon. In Tables 3 and 4 all of the compounds contain at least one benzylic carbon atom and in Table 5, all of the compounds except the naphthalenes and biphenyls contain at least
40   one benzylic carbon. None of the compounds set forth in Table 2 contain a benzylic carbon atom.

It is preferred to hydrorefine or hydrotreat the fuel fraction or distillate before selectively oxidizing the benzylic carbon atoms present therein. Such hydrorefining increases the number of benzylic carbon atoms present in said fraction. It also reduces the sulfur and nitrogen content of the fuel which may be necessary in order for same to meet required specifications, such as ASTM D 975. The hydrorefining is accomplished
45   by contacting the desired fraction, at elevated temperature and in the presence of hydrogen, with a suitable catalyst for a time sufficient to reduce the sulfur and nitrogen content thereof and increase the number of benzylic carbon atoms. The hydrorefined fraction is then selectively oxidized according to the process of this invention.

Suitable hydrorefining catalysts and conditions are well known to those skilled in the art. In general,
50   suitable catalysts will include one or more hydrogenating metal components selected from Group VIB and/or VIIIB of the Periodic Table on a suitable inorganic refractory metal oxide support, such as alumina, silica-alumina, etc. The support may contain components which provide certain cracking functionality, such as halogen, phosphorus, etc. A typical hydrorefining catalyst in commercial use today comprises a mixture of nickel and molybdenum supported on an alumina support. Typical hydrorefining conditions include a
55   temperature broadly ranging between about 150-500°C, preferably about 200-400°C, a pressure of from about 100-2,000 psi and preferably about 250-1,500 psi, a liquid hourly space velocity (LHSV) of from about 0.1 to 10 and preferably 0.5 to 6 v/v/hr. and a hydrogen gas rate of from about 200-10,000, preferably about 500-6000 SCF/B.

As set forth above, the process of this invention relates to a relatively low temperature process for selectively oxidizing the benzylic carbon atoms present in the aromatic and hydroaromatic components of the particular fuel fraction or middle distillate fraction that it is desired to improve the cetane number of. In accordance with this process, all or a portion, and preferably an extracted portion rich in aromatic and hydroaromatic compounds, will be contacted with oxygen or oxidant in the presence of a suitable catalyst at a relatively low temperature ranging from about 50-200°C, preferably 50-150°C and still more preferably 50-100°C for a time sufficient to oxidize at least a portion of the benzylic carbon atoms present in such fraction to the corresponding ketone.

The complete fuel fraction may be contacted with oxygen or an oxidant at relatively low temperature employing one or more catalysts useful in the process of this invention to selectively oxidize the benzylic carbon atoms present in the aromatic and hydroaromatic compounds present in the fraction to ketone compounds possessing higher cetane numbers. However, in some cases it will be preferred to extract the predominantly aromatic and hydroaromatic compounds containing such benzylic carbon atoms from the distillate or fraction employing a suitable extractant, such as SO_2, to form a raffinate and an extract rich in said aromatic and hydroaromatic hydrocarbon compounds and a raffinate reduced in aromatic and hydroaromatic hydrocarbons. The so-formed extract will then be contacted with oxygen or an oxidant according to the process of this invention. In the latter case, at least a portion of the oxidized extract will then be blended back into the raffinate in order to produce a fuel possessing improved cetane number.

By oxygen or suitable oxidant is meant air, pure oxygen, peroxides, hydroperoxides, persulfates, perchlorates, etc. By catalyst is meant either an oil or water soluble or insoluble compound, other than an oxide, of one or more catalytic metals selected from the group consisting of tin, antimony, lead, bismuth and transition metals of Groups IB, IIB, VB, VIB, VIIB and VIIIB of the Periodic Table. Illustrative but non-limiting examples of metals from these groups which will act as catalytic metals in the process of this invention include copper, zinc, vanadium, chromium, manganese, iron, cobalt and nickel. The catalytic process of this invention may be accomplished either heterogeneously or homogeneously. Thus, the catalytic metal compound may be an oil soluble metal salt, such as cobalt naphthenate, in which case the catalytic process will be accomplished homogeneously. On the other hand, the catalytic metal compound may be insoluble in both oil and water. In this case, the insoluble, non-oxide catalytic metal compound may be in a bulk form or supported on a suitable support material. In another embodiment, the catalyst may be in the form of a water soluble metal salt, such as copper sulfate, an aqueous solution of which will be dispersed in the fuel fraction to be selectively oxidized according to the process of this invention. Preferably the catalyst will be one or more oil or water soluble compounds.

The effect of cetane quality of molecular changes in compounds present in middle distillate fuel and their corresponding oxygenated compounds was determined by measuring their cetane blending numbers in a number of diesel fuels covering a range of compositions and cetane numbers. The measurement of cetane blending numbers, although more difficult to accomplish than simply measuring a cetane number, is important, since the oxidized compounds are used in blends and diesel fuels rather than as individual pure compounds. The effect of blending different compounds on the cetane number cannot be predicted based on the cetane number of the individual compounds, since currently there are no relatively accurate cetane blending-correlations. Moreover, the measurement of the cetane blending number was necessary, since compounds having a cetane number below about 20 cannot be measured in a cetane engine.

To minimize data scatter and the effect of random variables, a series of six measurements was conducted on each additive tested to determine the average cetane blending number. Base pools were prepared from refinery diesel blending stocks and blended to provide a range of cetane levels, i.e., a low cetane fuel (approximately 38 cetane number), a medium cetane fuel (approximately 41 cetane number) and a high cetane fuel (approximately 49 cetane number). The cetane numbers of each diesel pool were measured each time immediately prior to measuring the cetane number of the pure compound in the diesel pool. The cetane blending number of various pure compounds generally was determined at the 20 weight percent level in three different diesel pools and the results arithmatically averaged. A weight concentration rather than a volume concentration was used in preparing the blends because many pure compounds which were tested are solids at room temperature.

The cetane blending numbers were calculated according to the following linear blending equation:

$$CBN = \frac{CN_{Blend} - (1-X)CN_{Base}}{X}$$

where:

X = fraction of compound added to base pool to form blend;

5

CN = cetane number of the base or the blend, both measured in the cetane engine, with the blend being measured immediately after the base; and

CBN = calculated cetane blending number.

The effect of adding an alcohol, ketone, ester and ether functionality to a paraffin, cycloparaffin, aromatic and hydroaromatic hydrocarbon compound is shown in Tables I and II. In these tables, the average cetane blending numbers of the three pools are shown. The average cetane blending number of the pure compound is shown, with the change in average cetane number calculated preceded by a plus (+) for an increase in cetane number and preceded by a minus (-) for a decrease in cetane number. As shown in Table I, adding oxygen functionality to a hydroaromatic and to alkyl aromatics, in the benzylic position improved the cetane blending number. By contrast, as shown in Table II, adding oxygen functionality to a paraffin or cycloparaffin reduced the cetane blending number. As shown in Tables III and V, adding oxygen functionality to an alkyl aromatic in a non-benzylic side chain position or directly to the ring to form the phenol, reduced the cetane blending number.

The structure oxygenated and the location of the oxygen functionality also affects the cetane number of normal and branched paraffinic compounds. As shown in Table II, as an alcohol functionality is added to normal octane, the least loss of cetane quality occurs at the primary position and progressively greater loss of cetane quality occurs as the functionality is moved toward the center of the molecule. Similar effects also are shown in Table II for a branched paraffin, 2-ethyl hexane, where addition of the oxygen functionality causes the least loss at the primary position as compared to an interior position.

TABLE I

Effect of Oxygenate Functionality on Cetane Blending Number Δ of Aromatics and Hydroaromatics
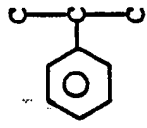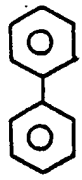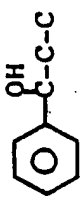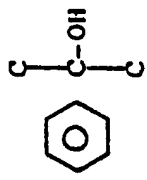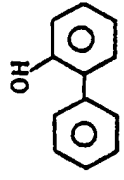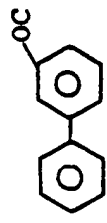
Change in Average Cetane Blending Number

Base Hydrocarbon Average Cetane Blending Number	Alcohol	Ketone	Methyl Ether
● n-Propylbenzene C—C—C (6.2)	1-Phenyl-1-propanol OH C—C—C Δ = +4.5		
● i-Propylbenzene C—C—C (9.4)	2-Phenyl-2-propanol C—C—OH C Δ = +3.6		
● Biphenyl (17.0)	2-phenyl phenol OH Δ = -22.6		o-Methoxybiphenyl OC Δ = -2.9

Table I - continued

Base Hydrocarbon Average Cetane Blending Number

1,2,3,4-Tetrahydro naphthalene (Tetralin)

(2.2)

• Fluorene

(6.0)

Alcohol

1,2,3,4-Tetrahydro 1-naphthol

OH

$\Delta = +12.8$

Ketone

α-Tetralone

O

$\Delta = +15.1$

9-Fluororenone

$\Delta = +14.1$

Methyl Ether

6-Methoxy-1,2,3,4-tetrahydro naphthalene

CH_3O

$\Delta = +3.7$

TABLE II

Effect of Oxygenate Functionality on Cetane Blending Number of Paraffins and Cycloparaffins

Change in Average Cetane Blending Number

Base Hydrocarbon Average Cetane Blending Number	Alcohol	Ketone	Ester	Ether
● n-Octane C-C-C-C-C-C-C-C (57.5)	1-octanol OH | C-C-C-C-C-C-C-C = - 16.7 2-Octanol OH | C-C-C-C-C-C-C-C Δ = -28.0	2-Octanone C-C-C-C-C-C-C-C Δ = -30.0	Methyl octanoate C-O-C-C-C-C-C-C-C Δ = -23.6	

Table II - continued

Ester	Ketone	Alcohol
Octyl Formate O ‖ C-O-C-C-C-C-C-C-C-C Δ = -17.0		3-octanol OH │ C-C-C-C-C-C-C-C Δ = -32.7 4-octanol OH │ C-C-C-C-C-C-C-C Δ = -38.2 2-Ethyl-1-hexanol C │ OH C │ │ C-C-C-C-C-C Δ = -7.1 4-Ethyl-3-hexanol OH C │ │ C │ C-C-C-C-C Δ = -22.6

Base Hydrocarbon Average Cetane Blending Number
● 2-Ethyl hexane C │ C │ C-C-C-C-C (35.9)

10
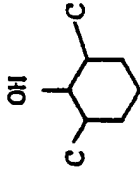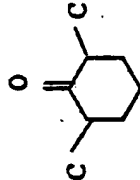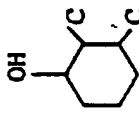
TABLE II – continued

Base Hydrocarbon Average Cetane Blending Number	Alcohol	Ketone	Ester
● 2,2,4-Trimethyl pentane	2,4,4-Trimethyl-1-pentanol		

2,2,4-Trimethyl pentane:

```
      C   C
      |   |
  C-C-C-C-C
      |
      C
```

(10.8)

2,4,4-Trimethyl-1-pentanol:

```
  C   C
  |   |
C-C-C-C-C-C-OH
      |
      C
```

Δ = –10.4

TABLE II – continued

Base Hydrocarbon Average Cetane Blending Number	Alcohol	Ketone	Ester	Ether
• 1,4-Dimethylcyclohexane (45.1)	2,6-Dimethylcyclo-hexanol $\Delta = -31.2$ 2,3-Dimethylcyclo-hexanol $\Delta = -26.8$	2-6, Dimethylcylo-hexanone $\Delta = -35.0$		
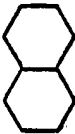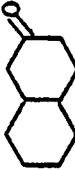
TABLE II – continued

Base Hydrocarbon Average Cetane Blending Number	Alcohol	Ketone	Ester	Ether

● Decalin (38.3)

Ketone: 2-Decalone Δ = -11.4

Improvements in the cetane numbers of certain aromatic and hydroaromatic, hydrocarbon compounds are dependent on the type and location of the functional group. The most effective compounds found for significantly increasing the cetane number are the hydroaromatics with the oxygenate functionality attached at a non-aromatic carbon, preferably to a benzylic carbon atom. As shown in Table III for alkyl benzenes

and in Table IV for alkyl naphthalenes, the maximum cetane number usually is achieved when the oxygenate functionality is attached to a benzylic carbon position. By contrast, as shown in Table V, when the oxygenate functionality is attached directly to the aromatic ring, a decrease in cetane number normally results. This is particularly the case when a hydroxy group is attached to the ring to form a phenol.

Table III

Effect of Oxygenate Addition to Alkyl Benzenes
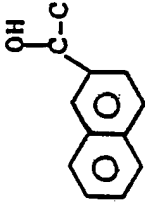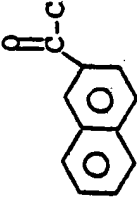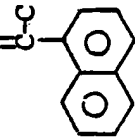
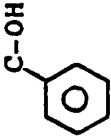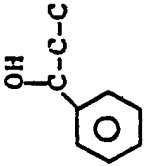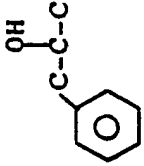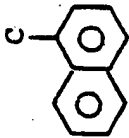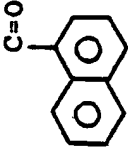| Base Hydrocarbon (Ave. Cetane Blending Number)	Change in Average Cetane Blending Number	
	Benzylic	Non-Benzylic
Toluene (8.3)	Benzyl Alcohol △ = +5.6	
N-Propylbenzene (6.2)	1-Phenyl-1-Propanol △ = +4.5	1-Phenyl-2-Propanol △ = -5.0

Table III - continued

Change in Average Cetane Blending Number

Base Hydrocarbon (Ave. Cetane Blending Number)	Benzylic	Non-Benzylic
● 1-Propylbenzene	2-Phenyl-2-Propanol	3-Phenyl-1-Propanol
(9.4)	$\Delta = +3.6$	$\Delta = -6.1$
		2-Phenyl-1-Propanol
		$\Delta = -7.8$

5

Table IV

Effect of Oxygenate Addition to Alkyl Naphthalenes

Change in Average Cetane Blending Number, Δ

Base Hydrocarbon (Average Cetane Blending Number)	Alcohol	Ketone or Aldehyde
● 1-Methyl Naphthalene (12.6)		1-Naphthaldehyde C=O $\Delta = +1.5$
● 2-Ethyl Naphthalene (5.0)	α Methyl-2-Naphthalene Methanol $\Delta = +17.6$	2-Acetonaphthone $\Delta = +7.8$
		1-Acetonaphthone $\Delta = +7.5$

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Table V

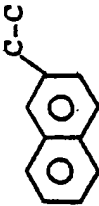### Effect of Methoxy and Hydroxy Addition
Directly to Aromatic Rings

Base Hydrocarbon (Average Cetane Blending Number)	Change in Average Cetane Blending Number of Oxygenated Compounds Relative to Hydrocarbon
● Toluene	P-Methylanisole
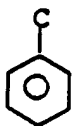
(8.3)   = -12.0
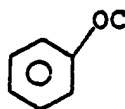
● Tetralin

6 Methoxy 1,2,3,4 Tetrahydro-naphthalene
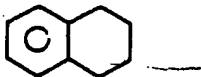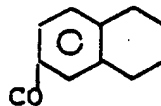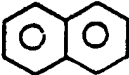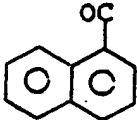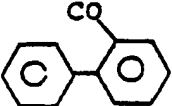
(2.2)   = +3.7

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Table V - continued

Base Hydrocarbon	Change in Average Cetane Blending Number of Oxygenated Compounds Relative to Hydrocarbon
• Naphthalene	1-Methoxynaphthalene
(21.9)	$\triangle$ = -12.2
• Biphenyl	0-Methoxybiphenyl
(17.0)	$\triangle$ = -2.9
Toluene	p-Cresol
(8.3)	$\triangle$ = -45.6
Indan	5-Indanol
(6.0)	$\triangle$ = -51.3

Table V - continued

Base Hydrocarbon	Change in Average Cetane Blending Number of Oxygenated Compounds Relative to Hydrocarbon
Tetralin	5,6,7,8 Tetrahydro -2- Naphthol

Tetralin

HO— 5,6,7,8 Tetrahydro -2-Naphthol

(2.2)   = -39.9

Biphenyl   2-Phenylphenol

(17.0)   = -22.6

When aromatic hydrocarbons are utilized, the maximum cetane number from oxygenation is achieved by converting polynuclear aromatics, such as naphthalenes, phenanthrenes and mixtures thereof, to the corresponding hydroaromatics. Although conversion of the multiple ring compounds to cycloparaffins would result in a still higher cetane number, the cost is high for the cetane improvement obtained. This is attributable to the greater hydrogen consumption, higher severity and higher pressure operation required to completely convert hydroaromatics to cycloparaffins. Therefore, when polynuclear aromatics are present, it can be seen that the present invention most economically can be practiced if the polynuclear aromatics are partially hydrogenated to hydroaromatics and oxygenated, rather than being completely hydrogenated to cycloparaffins prior to oxygenation. It can be seen that partial hydrogenation, such as that which occurs during hydrorefining, followed by oxygenation may produce a substantial increase in cetane at a lower cost per cetane number increase than complete hydrogenation of the polynuclear aromatic compounds to cycloparaffins.

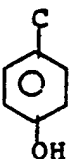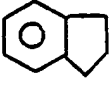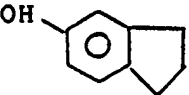Since aromatic-rich refinery feedstreams have been found to have relatively low cetane numbers, and since oxygenated aromatic compounds exhibit a sharp improvement in cetane, one particularly attractive method for improving the cetane number is to oxygenate refinery streams which have relatively high aromatics contents, such as liquid cat cycle oils, liquid cat heating oils, coker liquids, and mixtures thereof. Middle distillate fuels usually comprise a blend of refinery streams, such as virgin distillates, which have relatively high cetane numbers, and aromatics-rich process streams, which typically have relatively low cetane values. By oxygenating at least a portion of the aromatics-rich stream, increased quantities of the aromatics-rich stream can be blended with the virgin distillate to produce a middle distillate fuel having the same cetane number. Alternatively, the relative quantities of the aromatics rich stream and virgin distillate can be maintained constant, and the aromatics-rich stream oxygenated, thereby increasing the cetane number of the middle distillate product.

As previously stated, in some applications it may be desirable to separate refining streams comprising aromatics and paraffinic compounds into an aromatic-rich stream for subsequent oxygenation, and a paraffinic-rich stream. One method for selectively oxygenating hydroaromatics and aromatic compounds while not oxygenating the paraffinic and cycloparaffinic compounds is to separate the feedstock into a first fraction relatively rich in hydroaromatic and/or aromatic compounds and a second fraction relatively rich in paraffinic and/or cycloparaffinic compounds. Among the preferred methods for separating the feedstock into the first and second fractions are distillation, extraction and adsorption on a solid adsorbent, with the preferred method being extraction. The hydroaromatic and aromatic compounds may be selectively oxygenated by passing oxygen and/or air through the compounds or by the use of chemical oxygen donor compounds (oxidants).

The oxygenated aromatics and/or hydroaromatics preferably are blended with a fraction relatively rich in paraffin and/or cycloparaffins, such as a virgin distillate, to produce a middle distillate fuel having improved cetane. Alternatively, the oxygenated first fraction could be used as a diesel fuel alone.

The particular streams which are to be oxygenated, the extent to which each aromatic stream should be oxygenated and/or the amount which should be blended with a paraffinic-rich stream will be dependent, in part, on the solubility, melting point and boiling point of the oxygenated aromatics. Oxygenating typical aromatics frequently increases the melting point, boiling point and decreases the solubility of the aromatic components. Thus, the boiling point, melting point and solubility effects will be significant factors in preparing oxygenated middle distillate fuels. The hydrocarbon fuel, preferably may comprise about 0.5 to about 75 weight percent alkyl aromatics and/or hydroaromatics, more preferably about 2 to about 50 weight percent alkylaromatics and/or hydroaromatics and most preferably about 5 to about 30 weight percent alkylaromatics and/or hydroaromatics.

A series of tests were conducted on simulated aromatic-rich streams to demonstrate that the actual cetane blending number obtained when the aromatic fractions were replaced by their oxygenated analogs closely approximated the theoretical cetane blending number. These data are reported in Tables VI and VI. The data for Blend I reflects complete conversion of the aromatic compounds to ketones and alcohols, while the data for Blend II reflects complete conversion of the aromatics to alcohol.

Table VI

SIMULATED SELECTIVE OXIDATION OF AROMATIC RICH STREAM

Aromatic Rich Hydrocarbon Blend	Oxidized Aromatic Rich Blend I	Oxidized Aromatic Rich Blend II

Aromatic Rich Hydrocarbon Blend

Tetralin (40 wt.%) →O₂→ α-Tetralone → 1,2,3,4 Tetrahydro-1-Naphthol
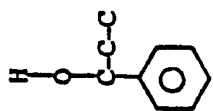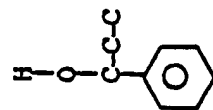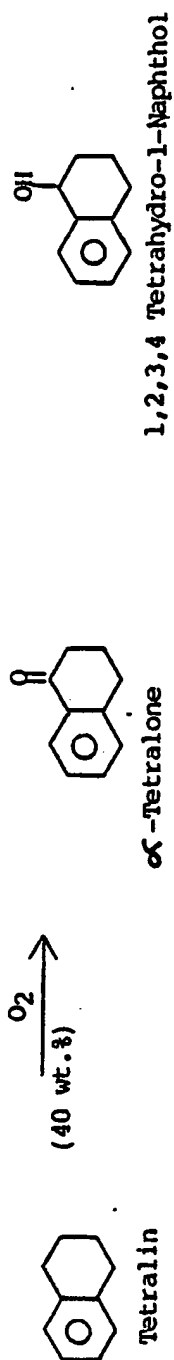
N-Propylbenzene (30%) →O₂→ 1-Phenyl-1-Propanol → 1-Phenyl-1-Propanol
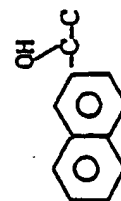
2-Ethylnaphthalene (5%) →O₂→ 2-Acetonaphthone → α-Methyl-2-Naphthalenemethanol
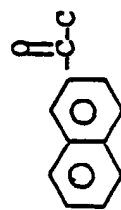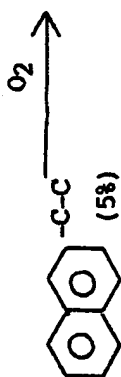
N-Decane (25%) → N-Decane → N-Decane

Table VII

Summary of Blend Results

Four Component Blend	Expected Cetane Blending Number	Measured Average Cetane Blending Number
Aromatic Rich Hydrocarbon	24	21.6
Oxidized Aromatic Rich Blend I (Ketone/Alcohol)	30	27.6
Oxidized Aromatic Rich Blend II (All Alcohol)	30	33.4

The invention will be further understood by reference to the Examples below.

EXAMPLES

In the examples, cetane number was determined using a standard cetane engine according to ASTM D-613. The feeds used in Examples 1, 2 and 3 each contain aromatic and/or hydroaromatic compounds containing benzylic carbon atoms.

Example 1

In this Example an SO_2 extract of a heavy aromatic naphtha was oxidized according to the process of this invention. Thus, 800 ml of the extract, 800 ml of acetonitrile, 177 grams of $CuSO_4 \cdot 5H_2O$, 1500 ml of distilled water and 1,000 grams of potassium persulfate were placed into a 5 liter, 3 necked flask equipped with an air driven mechanical stirrer, thermometer and water condenser. This mixture was rapidly heated to 65°C with stirring and then further slowly heated to 70-75°C. The mixture was then kept at a reflux temperature of 77-78°C with stirring for 3 hours after which it was cooled to room temperature using ice cooling.

The aqueous portion of the reacted mixture was removed by decanting and the oily product was washed with distilled water and the acetonitrile removed using a thin film evaporator. The remaining solids were rinsed with ether and the ether rinse added to the oil. This mixture was then washed with distilled water and the ether removed from the oxidized, oily product using a thin film evaporator. Elemental analysis of the oxidized product is set forth below.

Element	Weight Percent
C	86.14
H	9.93
N	<0.35
S	0.38

This oxidized product was then contacted with the potassium persulfate oxidant in the presence of an aqueous dispersion of the copper sulfate catalyst as set forth above. Thus, 1,265 ml of the previously oxidized oil was mixed with 1,000 ml acetonitrile and, 120 g copper sulfate pentahydrate and 540 g potassium persulfate and 1,200 ml water. This mixture was treated as above by heating rapidly to 65-70°C and then more slowly to 75°C, with the reaction mixture kept at a reflux temperature of 77-78°C with stirring for 6 1/2 hours. The reaction product was then left to cool to room temperature overnight. Cooled reaction mixture was then treated as above with respect to water washing, removal of solvent and ether washing of solids, etc. Elemental analysis of both the oxidized product and the unoxidized extract which served as the starting material are set forth below.

Element	Weight Percent	
	Starting Material	Oxidized Product
C	88.75	85.97
H	10.45	9.79
N	<0.35	<0.35
S	0.74	0.42
O	0.08	2.94

Comparison of this data with the data for the oxidized product resulting from the first extraction shows that the second oxidation did not result in any real significant change over the first oxidation.

Cetane Blending Number Results

The cetane blending number results are shown in Table VIII. These results definitely show the substantially increased cetane number results from blending the oxidized SO_2 extract with the base diesel pools as compared to the cetane number obtained by blending back a sample of the unoxidized SO_2 extract.

TABLE VIII

Cetane Blending Number of Samples

Base Diesel Pool	SO₂ Extract Heavy Aromatic Naphtha			Oxidized SO₂ Extract (Heavy Aromatic Naphtha)		
	Base Cetane Number	Blend Cetane Number (a)	Cetane Blending Number (b)	Base Cetane Number	Blend Cetane Number (a)	Cetane Blending Number (b)
Pool IV	38.4	33.8	15.4	39.2	36.7	26.7
Pool V	41.1	37.3	22.1	41.8	39.6	30.8
Pool VI	49.8	42.3	12.3	50.2	44.4	21.2
Pool IV	39.8	35.2	16.8	38.8	35.8	23.8
Average Cetane Blending Number			16.6			25.6

(a) Sample added to base pool at the 20 wt.% level and cetane numbers measured using the "back-to-back" technique.

(b) Cetane Blending Number = $\dfrac{\text{Blend Cetane Number} - 0.80\,(\text{Base Cetane Number})}{0.20}$

Example 2

In this experiment, 800 ml of a hydrorefined diesel fuel distillate was combined with 800 ml acetonitrile, 1,500 ml distilled water, 150 g of copper sulfate pentahydrate and 500 g of potassium per sulfate. This mixture was then heated, etc. following the procedure set forth in Example 1, except that an additional 100 g of potassium persulfate was added after 3 hours refluxing. The reaction product was then washed with water, etc. as set forth in Example 1. Elemental analysis of the oily product is set forth below.

Element	Weight Percent
C	87.36
H	11.49
N	<0.35
S	0.10
O	0.98

In contrast to this, elemental analysis of the oxygen content of the unoxidized extract showed an oxygen concentration of only 0.16%.

Samples of both the oxidized and unoxidized extract were then blended with various diesel pool stocks and the cetane and cetane blending numbers obtained. The results of this experiment are set forth in Table IX and again, clearly demonstrate the process of the present invention resulting in substantially increased cetane numbers obtained by blending the oxidized extract with the base diesel pool as opposed to blending back the unoxidized extract.

TABLE IX

CETANE BLEND NUMBERS OF SO_2 DIESEL FUEL EXTRACT

Sample Description	SO_2 Extract			Oxidized SO_2 Extract		
Base Diesel Pool	Base Cetane Number	Blend(a) Cetane Number	Cetane(b) Blending Number	Base Cetane Number	Blend Cetane Number	Cetane Blending Number
Pool 5	42.1	36.9	16.1	41.9	37.7(c)	20.9
Pool 6	49.3	43.3	19.3	49.7	48.1(c)	41.7
Pool 6	52.1	45.1	17.1	52.4	44.8(c)	14.4
Pool 6	52.3	42.3	2.3	51.5	44.7(c)	17.5
Average Cetane Blending Number			13.7			23.6

(a) Sample added to the Base Diesel Pool at the 20 vol. % level. The base and blend cetane numbers were measured using the "back-to-back" technique.

(b) Cetane Blending Number = $\dfrac{\text{Blend Cetane Number} - 0.80 \ (\text{Base Cetane Number})}{0.20}$

(c) Precipitates filtered from blend, 1.2 wt. % ppt in Pool 5 and 5.1-5.5 wt. % ppt in Pool 6.

Example 3

In this experiment, a heavy hydrocrackate was oxidized, again using the procedure set forth in Example 1. Thus, two separate batches of 800 ml of a heavy hydrocrackate were mixed with 800 ml acetonitrile, 1,500 ml of distilled water, 150 g copper sulfate pentrahydrate and 450 g of potassium per sulfate and placed in 25 liter, etc. flasks. The reaction mixture after being heated was cooled to room temperature and let stand over the weekend. The cooled reaction mixture was then decanted water washed, and solvent removed, etc. following the procedure in Example 1. Elemental analysis of the unoxidized and oxidized heavy hydrocrackate samples are set forth below.

Unoxidized Heavy Hydrocrackate

Element	Weight Percent
C	88.72
H	11.62
N	2 ppm
S	<1 ppm

Oxidized Heavy Hydrocrackate

Element	Weight Percent
C	87.22
H	10.86
N	<0.35
O	1.22

The cetane blend number results employing both the unoxidized and oxidized heavy hydrocrackate diesel fuel distillate are set forth Table X.

TABLE X

Cetane Blend Numbers of Baytown HHC

Sample Description	HHC			Oxidized HHC		
Base Diesel Pool	Base Cetane Number	Blend[a] Cetane Number	Cetane[b] Blending Number	Base Cetane Number	Blend[a] Cetane Number	Cetane[b] Blending Number
Pool 4	40.7	37.1	22.7	40.8	36.6	19.8
Pool 5	40.5	36.3	19.8	40.3	37.4(c)	25.6
Pool 5	42.0	36.4	14.0	41.1	37.8(c)	24.6
Pool 6	51.1	42.3	7.1	49.8	43.1(c)	16.3
Average Cetane Blending Number			15.9			21.6

(a) Sample added to the Base Diesel Pool at the 20 vol. % level. THe base and blend cetane numbers were measured using the "back-to-back" tecnique.

(b) Cetane Blending Number = $\dfrac{\text{Blend Cetane Number} - 0.80 \text{ (Base Cetane Number)}}{0.20}$

Example 4

In this Example, 5 grams of tetralin (Aldrich), 50 ml of toluene and 2.7 grams of n-decane were placed in a 3-neck, 100 ml flask equipped with a stirrer, thermometer, water condenser and air inlet bubbler and heated up to 60°C. Air was introduced and after 5 minutes, 0.10 grams of a cobalt naphthenate (6% Co) catalyst solution (Nuodex) was injected into the solution. Air was continually introduced, with stirring, at 60°C and samples were periodically withdrawn for gas-liquid chromotographic analysis.

Analysis revealed that the conversion of tetralin to tetralone was 33.4% complete after 9 hours; 47.7% complete after 10 hours; 54% complete after 13 hours and leveled off at about 57% after 14 hours.

Example 5

This experiment was similar to Example 4 and demonstrates the necessity for employing a catalyst in the process of this invention.

In this experiment, two batches each of 5 grams of tetralin (Aldrich), 50 ml of toluene and 2.7 grams of n-decane were placed in a 3-neck, 100 ml flask equipped with a stirrer, thermometer, water condenser and air inlet bubbler and heated up to 60°C. Air was continuously introduced into each flask and, after 5 minutes, 0.10 grams of a cobalt naphthenate (6% Co) catalyst solution (Nuodex) was injected into only one of the solutions. The air was continually introduced into each flask, with stirring, at 60°C and samples were withdrawn for gas-liquid chromotographic analysis and mass spec. analysis after 24 hours and 42 hours.

The analytical results revealed that without the catalyst present no tetralin was converted to tetralone after 42 hours. However, with the catalyst present, 57% of the tetralin was converted to tetralone after 42 hours.

Example 6

This experiment was similar to that of Example 5, except that the reactant was benzothiophene and this experiment was conducted in order to determine whether or not benzothiophene, a sulfur containing hydrocarbon compound, would react with the oxygen in the process of this invention.

Accordingly, two batches each of 5 grams of benzothiophene (Aldrich), 50 ml of toluene and 2.7 grams of n-decane were placed in a 3-neck, 100 ml flask equipped with a stirer, thermometer, water condenser and air inlet bubbler and heated up to 60°C. Air was introduced into each solution and, after 5 minutes, 0.10 grams of a cobalt naphthenate (6% Co) catalyst solution (Nuodex) was injected into each solution. Air was continually introduced into each flask, with stirring, at 60°C and samples were periodically withdrawn for gas-liquid chromatographic analysis and mass spec. analysis after 24 hours and 42 hours.

The analytical results revealed that in neither case, with or without the catalyst present, did the benzothiophene react with the oxygen even after 42 hours.

Claims

1. A process for increasing the cetane number of a middle distillate fuel fraction which contains aromatic and hydroaromatic hydrocarbon compounds having benzylic carbon atoms which comprises contacting said fraction with oxygen or an oxidant at a temperature below about 200°C in the presence of a catalyst for a time sufficient to selectively oxidize at least a portion of said benzylic carbon atoms to ketones.

2. A process as in claim 1 comprising the step of recovering a middle distillate fuel fraction of increased cetane number.

3. A process as in claim 1 or claim 2 in which the middle distillate fuel fraction of increased cetane number is blended with another middle distillate fuel fraction whose cetane number has not been increased.

4. The process of any one of claims 1 to 3 wherein said catalyst comprises at least one non-oxide compound of one or more catalytic metals selected from tin, antimony, lead, bismuth and transition metals of Group IB, IIB, VB, VIB, VIIB and VIIIB of the Periodic Table.

5. The process of any one of claims 1 to 4 wherein said fraction is a hydrorefined fraction.

6. The process of any one of claims 1 to 5 in which the catalyst is a soluble catalyst.

7. The process of any one of claims 1 to 6 wherein said catalyst is an oil-soluble metal salt.

8. The process of claim 7 wherein said oil-soluble metal salt is cobalt naphthenate.

9. The process of any one of claims 1 to 7 wherein said catalyst is water-soluble.

10. A process as in any one of claims 1 to 9 which comprises the steps of:

(a) extracting at least a portion of the aromatic and hydroaromatic hydrocarbon compounds present in said fraction to form an extract rich in said aromatic and hydroaromatic hydrocarbon compounds and a raffinate reduced in aromatic and hydroaromatic hydrocarbon compounds;

(b) contacting said extract formed in step (a) with oxygen or an oxidant in the presence of a catalyst at a temperature below about 200°C for a time sufficient to selectively oxidize at least a portion of the benzylic compounds in said extract to increase the cetane number thereof, and

(c) blending at least a portion of the oxidized extract formed in (b) with a middle distillate fuel fraction to increase its cetane number.